

1249728

# PATENT SPECIFICATION

(11) 1249728

(AC)

## NO DRAWINGS

(21) Application No. 50755/69 (22) Filed 15 Oct. 1969  
(31) Convention Application No. P 18 03 540.0  
(32) Filed 23 Oct. 1968 in  
(33) Germany (DT)  
(45) Complete Specification published 13 Oct. 1971  
(51) International Classification C 03 c 3/22, 21/00 // 3/04  
(52) Index at acceptance  
C1M 11B2 11B3 11C5 11C6 11C9 11F1 11F29 11F3  
11F33 11F34 11J3 11K8 13E 13J 13S2 D27



## (54) IMPROVEMENTS IN OR RELATING TO GLASS CERAMIC MATERIALS

(71) We, CARL-ZEISS-STIFTUNG, a Foundation established under the laws of Germany, of Heidenheim a.d. Brenz, Württemberg, Germany, trading as JENAER GLASWERK 5 SCHOTT & GEN., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention is concerned with a process for the production of transparent glass ceramic materials with low thermal linear expansion coefficients and high mechanical strengths which are produced by chemical strengthening.

15 In the invention, transparent glass ceramic materials containing metastable  $\beta$ -quartz solid solutions are provided by ion exchange with a surface layer whose composition is changed as compared with the interior of the glass ceramic material and which is under compressive stress, without, however, the transparency of the glass ceramic material, being altered.

20  $\beta$ -Quartz solid solutions are formed when, starting with pure  $\beta$ -quartz,  $\text{SiO}_2$  is replaced by  $\text{LiAlO}_2$  and/or  $\text{MgAl}_2\text{O}_4$  and/or  $\text{ZnAl}_2\text{O}_4$  and/or  $\text{AlPO}_4$ . If such crystal phases are separated by controlled crystallisation and with formation of glass ceramic materials from glasses, then their chemical compositions depend on the chemical composition of the glass from which they crystallise.  $\text{h}$ -quartz solid solutions are also referred to in the literature as  $\beta$ -eucryptite solid solutions.

25 Processes have been described which increase the mechanical strength of glass ceramic materials by ion exchange by means of salt melts (British Patent Specifications Nos. 1,105,433 and 1,105,434). These patent Specifications are concerned with the chemical

30 strengthening of glass ceramic materials, of which the main crystalline phases consist of cordierite, nepheline or  $\beta$ -quartz solid solutions. In glass ceramic materials containing cordierite,  $\text{Mg}^{2+}$  is replaced by  $2\text{Li}^+$  during the ion exchange operation, whereby  $\text{LiAl}$  silicates having lower thermal expansion co-

efficients as compared with cordierite are formed in the surface zones. With this process, compressive stresses are set up in these zones on cooling. In glass ceramic materials containing nepheline, the  $\text{Na}^+$  ion in the crystal lattice is replaced by the larger  $\text{K}^+$  ion during the ion exchange procedure. The higher elementary volume of the nephelines containing  $\text{K}^+$  in the surface layers of the treated materials places the latter under compressive stress. Finally, in  $\beta$ -quartz solid solutions which contain  $\text{Mg}^{2+}$  and which have relatively high  $\text{Mg}^{2+}$  contents (with  $\alpha$ -values of at least  $6 \times 10^{-7}/^\circ\text{C}$ ),  $\text{Mg}^{2+}$  is replaced by  $2\text{Li}^+$  in their surface zones on treating corresponding glass ceramic materials with  $\text{Li}_2\text{SO}_4$  melts. As a consequence, their expansion value falls, while their elementary volume increases. Consequently, compressive stresses are produced in the treated surface zones and these stresses lead to the increase in the mechanical strength of the glass ceramic material. Useful hardening effects were obtained in glass ceramics containing  $\beta$ -quartz solid solutions at temperatures between 800 and  $850^\circ\text{C}$ . In a second process which is described in both of the aforementioned British Patent Specifications, a hardening effect is produced on glass ceramic materials containing  $\beta$ -quartz solid solution if  $\text{K}_2\text{SO}_4/\text{KCl}$  melts are used as immersion baths at temperatures below  $800^\circ\text{C}$ .

35 It is the primary object of the present invention to develop a process for the production of transparent glass ceramic materials containing metastable  $\beta$ -quartz solid solutions and having low thermal linear expansion coefficients and high mechanical strength values by chemical strengthening. The chemical strengthening is to be carried out by ion exchange in the surface layers of transparent glass ceramic articles, the expansion values ( $\alpha_{20-300} 10^7 (1/^\circ\text{C})$ ) of which are preferably in the region of the value  $0 \pm 2$ , in time periods which economically can be accepted, in salt melts which contain  $\text{Li}^+$  and  $\text{K}^+$  and at temperatures between 650 and  $800^\circ\text{C}$ , without the trans-

50

55

60

65

70

75

80

85

90

parency of the materials being changed as a consequence and the high thermal shock resistance of the materials, given by the low thermal expansion, being changed.

5 The known processes for strengthening glass ceramic articles which contain  $\beta$ -quartz solid solutions only function with compositions having a particular MgO content, and no glass ceramic materials with zero expansion can be produced with these compositions. Optimum hardening effects are in addition reached in salt melts containing  $\text{Li}^+$  and  $\text{K}^+$  at temperatures between 800 and 850° C., that is, at temperatures at which melting vessels and furnace material are attacked to a stronger degree by the alkali melts than is the case in the temperature range between 650 and 800° C. used in the process of the invention.

10 It has been found that the ion exchange processes, which lead to the strengthening of transparent glass ceramic materials, proceed more quickly with increase of oxidic components contained in the  $\beta$ -quartz solid solutions of the glass ceramic materials besides  $\text{SiO}_2$ . The solid solution structures are then obviously less ordered, so that diffusion processes are facilitated. By using transparent glass ceramic materials, of which the  $\beta$ -quartz solid solutions show a relatively low  $\text{SiO}_2$  content, it has been possible to produce significant strengthening effects at temperatures between 650 and 800° C., with immersion times shorter than 10 hours. By this procedure was avoided or minimised the danger of transparent glass

15 20 25 30

ceramic materials becoming increasingly less transparent during the immersion operation, caused by increase in the average crystallite size of the crystal phase. Due to the lower immersion temperatures, the strengthening operation can technologically be handled more easily. The process mentioned in British Patent Specification No. 1,105,435, of strengthening the glass ceramic materials described by means of  $\text{K}_2\text{SO}_4/\text{KCl}$  melts, cannot be used, because  $\text{K}_2\text{SO}_4/\text{KCl}$  melts cloud the surfaces of the transparent glass ceramic materials. Furthermore, even after a short immersion time, cracks appear on surfaces of transparent glass ceramic materials, of which the expansion coefficients are smaller than  $5 \times 10^{-7}/^\circ\text{C}$ . Optical checking of such specimens indicates tensile stresses in the surface layers, into which  $\text{K}^+$  ions have diffused. The X-ray diffraction analysis of these zones which are under tensile stress indicates a substantial destruction of the  $\beta$ -quartz lattice of the crystal phase.

35 40 45 50 55

50 55

55 60 65

The choice of glass compositions which can be transformed into the transparent vitreous crystalline state is preferably made with regard to the zero expansion of the glass ceramic materials and also comparatively low  $\text{SiO}_2$  contents, on account of the good workability of the glasses and the high ion exchange speeds, which guarantee that the transparency of the glass ceramic materials after the strengthening operation is retained. The selected glass ceramic materials have the following chemical durability values:

70 hydrolytic class: I (according to DIN 12 111)  
 alkali class: II (according to DIN 52 322)  
 acid class: III (according to DIN 12 116)

(DIN — refers to German Industrial Standards).

75 80 85 90 95

As described in the literature,  $\text{SiO}_2$  in the lattice of the  $\beta$ -quartz solid solutions can be replaced by  $\text{LiAlO}_2$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{ZnAl}_2\text{O}_4$ , and  $\text{AlPO}_4$ . Favourable strengthening effects are produced by starting with glass ceramic materials of which the  $\beta$ -quartz solid solutions contain a large quantity of  $\text{MgAl}_2\text{O}_4$  and treating these with lithium salt melts. With increasing  $\text{MgAl}_2\text{O}_4$  content, however, the expansion values of the glass ceramic materials also increase. For the transparent glass ceramic materials used in the invention, of which the expansion values are close to the value 0, their MgO content should not exceed the value of 2% by weight. For the ion exchange procedure of  $\text{Mg}^{2+} \rightleftharpoons 2\text{Li}^+$  in lithium salt melts, which produces a strengthening effect, and in contrast to the examples of the said British patent Specification 1,105,435, less  $\text{Mg}^{2+}$  is thus present in the transparent glass ceramic material with low expansion (see hereinafter Examples 1 to 5, Table 1). It has now been found, by measuring concentration gradients

100 105 110 115

by means of an electron microprobe, that the  $\text{Mg}^{2+} \rightleftharpoons 2\text{Li}^+$  exchange and the  $\text{Zn}^{2+} \rightleftharpoons 2\text{Li}^+$  exchange proceed at approximately the same speed when surfaces of glass ceramic materials of the indicated compositions are brought into contact with the lithium salt melts. Consequently, also significant strengthening effects on glass ceramic materials were produced in lithium salt melts which show appreciable  $\text{ZnO}$  proportions as well as little MgO (less than 1.0% by weight in Examples 4 and 5, Table 1). This discovery was very important for the purpose as initially described, since also with relatively high  $\text{ZnO}$  contents (see Example 5, Table 1), it is possible to produce transparent glass ceramic materials with zero expansion. If  $\text{SiO}_2$  in  $\beta$ -quartz solid solutions is further replaced (apart from  $\text{LiAlO}_2$ ,  $\text{MgAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$ ) by  $\text{AlPO}_4$ , less ordered solid solutions with decreasing  $\text{SiO}_2$  content are always obtained.

Transparent glass ceramics with zero expansion can also be obtained if the  $\beta$ -quartz

solid solutions contained in them have appreciable proportions of  $\text{AlPO}_4$  (Examples 2—4, Table 1). It was once again established by microprobe testing of surface layers of such glass ceramic materials, which has been treated with salt melts containing  $\text{Li}^+$  and  $\text{K}^+$ , that a penetration of  $\text{K}^+$  ions into the surface of the glass ceramic material took place increasingly quickly at temperatures between 650 and 800° C., if the specimens of glass ceramic materials had increasing  $\text{P}_2\text{O}_5$  contents. The strengthening effects were observed with correspondingly lower temperature or shorter time as the  $\text{SiO}_2$  content of the specimens was made less and the  $\text{P}_2\text{O}_5$  content was made more. It has still not been possible to explain the mechanism of the strengthening effect of penetration of  $\text{K}^+$  into the surfaces of the transparent glass ceramic materials.

According to this invention we provide a process for the production of transparent glass ceramic materials which contain metastable  $\beta$ -quartz solid solutions, which process comprises treating a glass ceramic material having a weight percentage composition of

30	50 — 65 $\text{SiO}_2$
	21 — 28 $\text{Al}_2\text{O}_3$
	0 — 10 $\text{P}_2\text{O}_5$
	1.5 — 5 $\text{Li}_2\text{O}$
	0 — 2 $\text{MgO}$
	0 — 8 $\text{ZnO}$
	0.5 — 5 $\text{TiO}_2$
	1 — 3 $\text{ZrO}_2$
	0 — 1 $\text{Na}_2\text{O}$
35	0.5 — 1 $\text{As}_2\text{O}_3$ , and wherein

the ratio by weight according to synthesis of

$\text{SiO}_2$ :  $(\text{AlPO}_4 + \text{LiAlO}_2 + \text{MgAl}_2\text{O}_4 + \text{ZnAl}_2\text{O}_4)$  is 1.2—2.1:1

the sum of  $\text{SiO}_2 + \text{AlPO}_4 \leq 71\%$  by weight

the sum of  $\text{MgO} + \text{ZnO} \geq 2\%$  by weight

the sum of  $\text{SiO}_2 + \text{AlPO}_4 + \text{ZnAl}_2\text{O}_4 + \text{MgAl}_2\text{O}_4 + \text{LiAlO}_2 \geq 90\%$  by weight,

the remainder comprising the nucleus-forming components  $\text{TiO}_2 + \text{ZrO}_2$  and the refining agent  $\text{As}_2\text{O}_3$  with or without  $\text{Na}_2\text{O}$ , with a salt melt containing  $\text{Li}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  for an immersion time between 1 and 10 hours and at treatment temperatures between 650 and 800° C., for producing strength-improving compressive stress layers on the cooled glass ceramics. Preferably the said treatment temperature is between 700 and 750° C. The said transparent glass ceramic material preferably contains both  $\text{MgO}$  and  $\text{ZnO}$  and preferably both  $\text{Na}_2\text{O}$  and  $\text{As}_2\text{O}_3$ . Advantageously the transparent glass ceramic material contains more than 5 percent by weight of  $\text{P}_2\text{O}_5$ . Generally the salt melt contains more than 50% by weight of  $\text{Li}_2\text{SO}_4$  and preferably at least twice the amount by

weight of  $\text{Li}_2\text{SO}_4$  to the amount of  $\text{K}_2\text{SO}_4$ .

In one form of process embodying this invention, the temperature at which ion exchange is allowed to take place in a surface layer of the glass ceramic material produced in accordance with this invention in a salt melt containing  $\text{Li}_2\text{SO}_4/\text{K}_2\text{SO}_4$  is adapted to the  $\text{SiO}_2$  content of the glass ceramic material, and in such a way that a said glass ceramic material with a  $\text{SiO}_2$  content less than 60% by weight is treated in the lower region of the temperature range which is between 650 and 750° C., and the said glass ceramic material with  $\text{SiO}_2$  content greater than 60% by weight is treated in the upper region of the temperature range which is between 750 and 800° C.

Expediently, the  $\text{K}^+$  content of the  $\text{Li}_2\text{SO}_4/\text{K}_2\text{SO}_4$  salt melt, with which ion exchange is carried out in a surface layer of the glass ceramic material, is so adjusted that the  $\text{K}_2\text{SO}_4$  content of the melt amounts to 30% by weight when the glass ceramic material contains, less than 60% by weight of  $\text{SiO}_2$ , and amounts to 10% by weight of  $\text{K}_2\text{SO}_4$  when the glass ceramic material contains more than 60% by weight of  $\text{SiO}_2$ .

In another form of process embodying this invention the temperature level of the ion exchange procedure is divided into two stages for avoiding or minimising destruction of the surfaces of a said strengthened glass ceramic material, and in such a way that the glass ceramic article to be strengthened is initially kept for 1 hour in the salt melt at a temperature which is 50—100° C. below the final strengthening temperature, is then heated at 5° C/min. in this melt to the strengthening temperature and remains at this temperature in the melt bath until a sufficient increase in mechanical strength is obtained.

The compositions of the salt melts used for strengthening the glass ceramic materials according to the process of the invention can be varied, for instance, within the limits of 60% by weight  $\text{Li}_2\text{SO}_4/40\%$  by weight  $\text{K}_2\text{SO}_4$  to 90% by weight  $\text{Li}_2\text{SO}_4/10\%$  by weight  $\text{K}_2\text{SO}_4$ . The more  $\text{K}^+$  which is contained in the salt melt in this concentration range, the lower are the immersion temperatures which are required in order to observe distinct strengthening effects. Nevertheless, it was also noticed that, by increasing the  $\text{K}^+$  content of the salt melts, the danger of destruction in the  $\beta$ -quartz solid solutions in the diffusion layer of the treated glass ceramics increases, the strengthening effects being again decreased.

It was also noticed that, during the strengthening operation, the specimens of glass ceramic material often split at the treated surfaces. Systematic tests showed that initially a tensile stress was developed in the surface zones of the glass ceramic materials as described, after they came into contact with  $\text{Li}_2\text{SO}_4/\text{K}_2\text{SO}_4$  melts, if the specimens were removed

from the melts and cooled. The surface zones of such specimens treated for only a short time showed many cracks. If the specimens of glass ceramic material were in the salt melt 5 for 30 minutes to 2 hours (depending on the composition of the specimen, the composition of the melt and the immersion temperature), cooled, specimens then showed increasingly compressive stresses in the surface layers. The 10 surfaces remained undamaged. This phenomenon can be explained as follows: with the commencement of the penetration of  $\text{Li}^+$  ions  $\text{K}^+$  ions may also penetrate into the lattice of the quartz solid solutions and the migration 15 of the  $\text{Mg}^{++}$  and  $\text{Zn}^{++}$  ions from the solid solution lattice, the said lattice is initially seriously damaged, this occurring to a greater extent as the ion exchange procedure is started more quickly at relatively high temperature. 20 It is obvious that this procedure, which is connected with changes in volume in the zones concerned, is a reason for the destruction of the surfaces. Finally, since scarcely any  $\text{Zn}^{++}$  and  $\text{Mg}^{++}$  is still present in the surface layers, 25 the solid solutions are again oriented and the compressive stress zones can be built up. In order to prevent this cracking during the strengthening operation, it is necessary to avoid a too sudden collapse of the solid solution 30 lattice in the surface layers of the specimen of treated glass ceramic material. For this purpose, the strengthening operation is preferably started at about 50—100° C. below the final temperature at which the ion exchange is to 35 take place, the specimen and melt are kept for 1 to 2 hours at this low temperature and then the immersion temperature is only increased at 2 to 5°C/minute to the final value. Using this process, the specimens of glass ceramic 40 material withstand the immersion operations without external damage.

In order to ascertain the increase in the mechanical strength of transparent glass ceramics strengthened by ion exchange in 45  $\text{Li}^+/\text{K}^+$  salt melts, specimens with a thickness of 1 mm and polished on both sides were brought into contact with  $\text{Li}_2\text{SO}_4/\text{K}_2\text{SO}_4$  melts at temperatures between 650 and 800° C. The salt melts were in ceramic tanks or 50 vessels, which in their turn stood in a muffle made of fire-resistant steel. The muffle in its turn was disposed in an electrically heated furnace which could be controlled according to a programme. In the muffle chamber, a 55 constancy of temperature better than  $\pm 5^\circ \text{C}$ . could be obtained. After the immersion time had ended, the round discs were removed from the hot melt, a procedure which they withstood, because of their extremely high temperature shock resistance, and freed by means of hot water from the residues of adhering  $\text{Li}^+/\text{K}^+$  salt. It could be judged from the transparent specimens polished on both sides whether the treatment of the specimens with the salt melt had altered their transparency and their surface quality. With satisfactory strengthened round discs with a diameter of 40 mm and a thickness of 1 mm, which had been treated on both sides with grade 600 emery, the bending strength was measured by means of a bending test machine made by Messrs. ZWICK (model Z 2 2A). For this purpose, the specimens were loaded with a constantly increasing force until a break occurred. From the breaking load  $P$  and the specimen thickness  $h$ , the bending tensile strength  $\delta$  in accordance with  $\delta = 1.4 \frac{P}{h^2}$  60 is obtained when the ratio of the diameter of the pressing surface to the mean diameter of plate and support is equal to 1/5. For the tensile strength values which are given in the following Examples, always 10 specimens, which were subjected to the same test conditions, were measured and the arithmetic mean was indicated. The range of difference in the measured values was a maximum of  $\pm 15\%$ . In order to establish whether the strengthening effect obtained on the specimens of glass ceramic material satisfies the demands when using glass ceramic material treated in similar manner, discs of glass ceramic material were treated, after the strengthening operation, in a cup of a ball mill without balls for 15 minutes at 120 r.p.m. with grade 320 emery and the tensile strength was measured. It was found that strengthened specimens, after this operation, then showed no or only an insignificant reduction in strength, when the compressive stress zones in their surfaces exceeded a thickness of  $80 \mu$ . The strengthening effects occurring with variation of the chemical composition of the glass ceramic materials and of the salt melts, of the different immersion temperatures and immersion times, were judged under the microscope by measuring the compressive stress values in the surfaces of the treated glass ceramic materials, the thickness of the compressive stress zones and the stress gradients. It was only from test specimens which under the microscope showed high compressive stress values with sufficient thickness of the stress zones that a sufficient number was produced for carrying out the bending tensile strength 65 70 75 80 85 90 95 100 105 110 measurements.

TABLE 1

Example No.	1	2	3	4	5
SiO <sub>2</sub>	54.3	53.0	55.4	58.1	63.6
Al <sub>2</sub> O <sub>3</sub>	26.0	26.3	25.2	22.9	21.9
P <sub>2</sub> O <sub>5</sub>	7.8	7.8	7.9	7.3	—
LiO <sub>2</sub>	4.0	3.8	3.7	3.5	2.9
MgO	1.6	1.1	1.0	0.7	0.9
ZnO	0.9	2.2	1.4	1.7	6.2
TiO <sub>2</sub>	2.3	2.8	2.3	2.9	1.8
ZrO <sub>2</sub>	1.9	1.9	1.9	1.7	1.9
Na <sub>2</sub> O	0.5	0.6	0.5	0.6	—
As <sub>2</sub> O <sub>3</sub>	0.7	0.5	0.7	0.6	0.8
Nucleating temp.	720°C	720°C	720°C	720°C	740°C
Nucleating time	4 hours	2 hours	10 hours	2 hours	1 hour
Cryst. temp.	830°C	830°C	830°C	830°C	829°C
Cryst. time	2 hours	3 hours	3 hours	3 hours	3 hours
Colour	yellowish	yellowish	yellowish	yellowish	yellowish
Transparency	Tyndall (very weak)	clear	clear	clear	clear
$\alpha 20-300/10^7$ (1/°C)	+2	0	0	-0.5	0

The results of a number of tests for chemical hardening of these glass ceramic materials are set out below on the basis of 5 the glass ceramic compositions listed in Table 1. The tensile strength values indicated in Tables 2 to 6 are a standard for the strengthening effect, when it is considered that the tensile strength of untreated specimens of glass 10 ceramic material of the composition indicated in Table 1, when they are measured under the same conditions as the strength of the specimens treated with salt melts, amounts to about 850 to 900 kp/cm<sup>2</sup>.

15 EXAMPLE 1:

A glass of the composition of Example 1 in Table 1 was melted in a quartz crucible at temperatures in the region of 1600° C., refined, cooled by stirring to 1400° C., poured 20 into a mould and cooled. The unstressed glass was heated at 1°C/min to 720° C., kept at

this temperature for 4 hours, then brought at 1°C/min to 830° C., kept at this temperature for 2 hours, and by being removed from the electrically heated furnace, it was cooled in air.

A transparent glass ceramic containing metastable  $\beta$ -quartz solid solutions as main crystallisation product was formed in this way. Discs with a diameter of 40 mm and a thickness of 1 mm, with surfaces ground with grade 600 emery, were obtained from this material and strengthened according to the conditions described in Table 2. It was shown that significant strengthening effects already occurred at temperatures in the region of 650° C. when the

35 K<sup>+</sup> content of the melts was increased. If the K<sub>2</sub>SO<sub>4</sub> content of the melts was raised to above 30% by weight, the strengthening effects decreased again. Untreated discs of this glass ceramic material showed bending tensile strengths of about 900 kp/cm<sup>2</sup>.

25

30

35

40

TABLE 2

Glass ceramic composition No. (see Tab. 1)	Melt bath compositions (% by weight)	Immersion temperatures (°C)	Immersion times (hour)	bending tensile strength (kp/cm <sup>2</sup> )
1	90 Bi <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	650	6	1 400
1	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	700	4	2 900
1	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	700 for 1 hour followed by 750 for 4 hours		3 900
1	70 Li <sub>2</sub> SO <sub>4</sub> 30 K <sub>2</sub> SO <sub>4</sub>	650	4	3 000

## EXAMPLE 2:

5 A glass with the composition 2 (Table 1) was produced as described in Example 1 and a glass ceramic material was obtained therefrom according to the temperature programme indicated in Table 1 for Example 2. The results of some strengthening tests carried out on this transparent glass ceramic material with 10 zero expansion, using test elements such as those described in the preceding examples, are set out in Table 3. Untreated test elements of this glass ceramic material showed bending

15 tensile strengths of 850 kp/cm<sup>2</sup>. Plates polished on both sides, which had been strengthened in accordance with the conditions of the third experiment (Table 3) were thereafter subjected to a temperature of 650° C. for 200 hours. The compressive stress zones were tested optically, before and after the experiment. The stress ratios and thus the strengthening conditions had not been appreciably altered. At 20 temperatures of 750° C., the stresses on the surfaces of the specimens were clearly reduced after 200 hours.

15

20

25

TABLE 3

Glass ceramic composition No. (see Tab. 1)	Melt bath compositions (% by weight)	Immersion temperatures (°C)	Immersion times (hour)	bending tensile strength (kp/cm <sup>2</sup> )
2	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	700 for 0.5 hour followed by 750 for 0.5 hour		2 000
2	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	700 for 1 hour followed by 750 for 1 hour		3 000
2	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	700 for 1 hour followed by 750 for 4 hours		3 200

30 It is clear from the results of the immersion tests of this Example that, under the conditions chosen, immersion times of altogether only two hours produce strengthening effects by a factor 3.5, whereas longer immersion

times only produce insignificant improvements in the strengthening effect.

## EXAMPLE 3:

A transparent glass ceramic material containing  $\beta$ -quartz solid solution and with a zero

35

expansion, in accordance with composition 3 (ground on both sides with grade 600 emery) 5  
(Table 1) was obtained from the corresponding initial glass by the ceramising programme  
indicated for Example 3 in Table 1, test discs were produced therefrom and strengthening  
tests were carried out according to the conditions indicated in Table 4.

TABLE 4

Glass ceramic composition No. (see Tab. 1)	Melt bath compositions (% by weight)	Immersion temperatures (°C)	Immersion times (hour)	bending tensile strength (kp/cm <sup>2</sup> )
3	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	700 for 1 hour followed by 800 for 6 hours		1 800
3	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	700 for 1 hour followed by 750 for 4 hours		3 000
3	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	700	4	2 300
3	70 Li <sub>2</sub> SO <sub>4</sub> 30 K <sub>2</sub> SO <sub>4</sub>	700 for 1 hour followed by 750 for 6 hours		4 500
3	70 Li <sub>2</sub> SO <sub>4</sub> 30 K <sub>2</sub> SO <sub>4</sub>	700	4	3 300

10 From the results which are set out in Table 4, it is seen that the use of immersion temperatures in the region of 800° C. for the glass ceramic composition 3 does not produce such good strengthening effects by comparison 25  
15 with the use of lower strengthening temperatures. Similar observations were made with immersion tests of the compositions 1 and 2, but were not indicated in detail. Untreated discs of glass ceramic material of the composition 3 showed bending strength values of 30  
20 about 900 kp/cm<sup>2</sup>. The maximum strengthening effect achieved in this series of experiments amounts to 5.

## EXAMPLE 4:

A transparent glass ceramic material containing  $\beta$ -quartz solid solution and with a zero expansion, in accordance with composition Example 4 (Table 1) was obtained from the corresponding initial glass, using the temperature programme indicated in Table 1. Strengthening tests were carried out under the conditions indicated in Table 5 on test discs with a thickness of 1 mm and a diameter of 40 mm, which had been ground on both sides with grade 600 emery. Untreated test discs of this glass ceramic material had a tensile strength of 930 kp/cm<sup>2</sup>. 35

TABLE 5

Glass ceramic composition No. (see Tab. 1)	Melt bath compositions (% by weight)	Immersion temperatures (°C)	Immersion times (hour)	Bending tensile strength kp/cm <sup>2</sup>
4	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	750	1	1 700
4	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	750 for 1 hour followed by 800 for 2 hours		2 000
4	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	750 for 1 hour followed by 800 for 3 hours		2 300
4	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	750 for 1 hour followed by 800 for 4 hours		2 700
4	70 Li <sub>2</sub> SO <sub>4</sub> 30 K <sub>2</sub> SO <sub>4</sub>	750	6	3 000
4	70 Li <sub>2</sub> SO <sub>4</sub> 30 K <sub>2</sub> SO <sub>4</sub>	750 for 1 hour followed by 800 for 2 hours		2 300
4	70 Li <sub>2</sub> SO <sub>4</sub> 30 K <sub>2</sub> SO <sub>4</sub>	750 for 1 hour followed by 800 for 6 hours		2 800

It also becomes clear from the tests which are described in Table 5 that useful strengthening effects are to be produced on glass ceramic materials of the composition 4 (Table 1) at immersion temperatures between 750 and 800° C. with immersion times shorter than 10 hours.

EXAMPLE 5:  
10 A transparent glass ceramic material containing  $\beta$ -quartz solid solutions and with a

zero expansion, according to composition of Example 5 (Table 1) was obtained from the corresponding initial glass by the temperature programme indicated in Table 1. Test discs were subjected to the strengthening conditions set out in Table 6. Untreated discs of glass ceramic material of this composition showed the bending tensile strength values of 900 kp/cm<sup>2</sup>.

15

20

TABLE 6

Glass ceramic composition No. (see Tab. 1)	Melt bath compositions (% by weight)	Immersion temperatures (°C)	Immersion times (hour)	Bending tensile strength kp/cm <sup>2</sup>
5	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	750 for 1 hour followed by 800 for 4 hours		2 000
5	90 Li <sub>2</sub> SO <sub>4</sub> 10 K <sub>2</sub> SO <sub>4</sub>	750 for 1 hour followed by 800 for 6 hours		2 500

A raising of the  $K^+$  concentration of the salt melts, when strengthening the glass ceramic material according to Example 5, did not lead to the possibility of using lower immersion temperatures.

If the strengthening effects which have been shown in Examples 1—5 are considered, in conjunction with the immersion temperatures and the glass ceramic compositions, the rule which is to be clearly recognised is that the higher the  $SiO_2$  content in the composition of the glass ceramic, the higher are the immersion temperatures which are necessary for producing equivalent strengthening effects. Glass ceramic materials with 54% by weight of  $SiO_2$  can be hardened at 650° C. (Example 1) in accordance with the process described, but for glass ceramic materials with about 64% by weight of  $SiO_2$ , strengthening temperatures of or approaching 800° C. are necessary. These Examples have been chosen in order clearly to bring out the dependence of the effective immersion temperatures on the  $SiO_2$  content of the transparent glass ceramic materials.

**WHAT WE CLAIM IS:—**

1. A process for the production of transparent glass ceramic materials which contain metastable  $\beta$ -quartz solid solutions, which process comprises treating a glass ceramic material having a weight percentage composition of
 

35	50 — 65 $SiO_2$
	21 — 28 $Al_2O_3$
	0 — 10 $P_2O_5$
	1.5 — 5 $Li_2O$
	0 — 2 $MgO$
	0 — 8 $ZnO$
	0.5 — 5 $TiO_2$
40	1 — 3 $ZrO_2$
	0 — 1 $Na_2O$
	0.5 — 1 $As_2O_3$ , and wherein

the ratio by weight according to synthesis of:  $SiO_2$ : ( $AlPO_4$  +  $LiAlO_2$  +  $MgAl_2O_4$  +  $ZnAl_2O_4$ ) is 1.2—2.1:1

the sum of  $SiO_2$  +  $AlPO_4$  ≤ 71% by weight

the sum of  $MgO$  +  $ZnO$  ≥ 2% by weight

the sum of  $SiO_2$  +  $AlPO_4$  +  $ZnAl_2O_4$  +  $MgAl_2O_4$  +  $LiAlO_2$  ≥ 90% by weight,

the remainder comprising the nucleus-forming components  $TiO_2$  +  $ZrO_2$  and the refining agent  $As_2O_3$  with or without  $Na_2O$ , with a salt melt containing  $Li_2SO_4$  and  $K_2SO_4$  for an immersion time between 1 and 10 hours and at treatment temperatures between 650 and 800° C., for producing strength-improving compressive stress layers on the cooled glass ceramics.

60 2. A process according to Claim 1, wherein the said treatment temperature is between 700 and 750° C.

3. A process according to Claim 1, wherein the temperature at which ion exchange is allowed to take place in a surface layer of the glass ceramic material specified in Claim 1 in a salt melt containing  $Li_2SO_4$ / $K_2SO_4$  is adapted to the  $SiO_2$  content of the glass ceramic material, and in such a way that a said glass ceramic material with a  $SiO_2$  content less than 60% by weight is treated in the lower region of the temperature range which is between 650 and 750° C., and the said glass ceramic material with a  $SiO_2$  content greater than 60% by weight is treated in the upper region of the temperature range which is between 750 and 800° C.

4. A process according to any preceding Claim, wherein the  $K^+$  content of the  $Li_2SO_4$ / $K_2SO_4$  salt melt, with which ion exchange is carried out in a surface layer of the glass ceramic material, is so adjusted that the  $K_2SO_4$  content of the melt amounts to 30% by weight when the glass ceramic material contains less than 60% by weight of  $SiO_2$ , and amounts to 10% by weight of  $K_2SO_4$  when the glass ceramic material contains more than 60% by weight of  $SiO_2$ .

5. A process according to any preceding claim wherein the ion exchange procedure is divided into two stages for avoiding or minimising destruction of the surfaces of a said strengthened glass ceramic material, and in such a way that the glass ceramic articles to be strengthened is initially kept for 1 hour in the salt melt at a temperature which is 50—100° C. below the final strengthening temperature, is then heated at 5° C./min. in this melt to the strengthening temperature and remains at this temperature in the melt bath until a sufficient increase in mechanical strength is obtained.

6. A process according to any preceding claim, wherein the said transparent glass ceramic material contains both  $MgO$  and  $ZnO$ .

7. A process according to any preceding claim, wherein the said transparent glass ceramic material contains both  $Na_2O$  and  $As_2O_3$ .

8. A process according to any preceding claim, wherein the said transparent glass ceramic material contains more than 5 percent by weight of  $P_2O_5$ .

9. A process according to any preceding claim, wherein the salt melt contains more than 50 percent by weight of  $Li_2SO_4$ .

10. A process according to Claim 9, wherein the salt melt contains at least twice the amount by weight of  $Li_2SO_4$  to the amount of  $K_2SO_4$ .

11. A process according to Claim 1 substantially as herein described and exemplified.

12. A transparent glass ceramic material when obtained by the process claimed in any preceding claim.

---

MEWBURN ELLIS & CO.,  
Chartered Patent Agents,  
70-72 Chancery Lane,  
London, W.C.2.  
Agents for the Applicants.

---

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.